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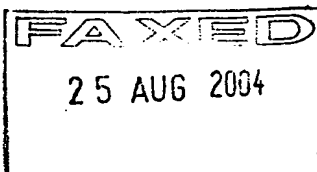
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DTG Rec'd PCT/STO 2.8 FEB 2005  
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Via Fax & Courier  
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August 25, 2004



Dear Sir

Re : RESPONSE TO THE WRITTEN OPINION UNDER RULE 66.3  
PCT International Application No. PCT/IN03/00278  
International Filing Date : 22.08.2003  
Applicant : Tata Institute of Fundamental Research, et al  
Title : CHROMIUM DIOXIDE ( $\text{CrO}_2$ ) AND COMPOSITES OF CHROMIUM  
DIOXIDE AND OTHER OXIDES OF CHROMIUM SUCH AS  $\text{CrO}_2/\text{Cr}_2\text{O}_3$   
AND  $\text{CrO}_2/\text{Cr}_2\text{O}_5$  AND PROCESS FOR MANUFACTURING THE SAME  
Priority Date : 29.08.2002  
Agent's File Ref. : FPAA240PCT

The present invention relates to substantially pure  $\text{CrO}_2$  having saturation magnetization of above 110 emu/gm preferably at least 115 emu/gm. The  $\text{CrO}_2$  has negative magneto resistance of at least 0.5% near room temperature at 2 Tesla. The invention further relates to composites  $\text{CrO}_2 / \text{Cr}_2\text{O}_3$  and  $\text{CrO}_2 / \text{Cr}_2\text{O}_5$  both having magneto resistance of at least 0.5% near room temperature at 2 Tesla and a process of manufacture of the  $\text{CrO}_2$  and its composites wherein intermediate  $\text{Cr}_8\text{O}_{21}$  is formed and then transformed into  $\text{CrO}_2$  and its composites by modulating temperatures.

Jianbiao Dai and Jinke Tang teaches polycrystalline  $\text{CrO}_2$  with saturation magnetization of 110 emu/gm. Further such  $\text{CrO}_2$  is commercially available which is known to be prepared by method where pressure is a control factor.

GB 1 274 880 A teaches a process for preparation of  $\text{CrO}_2$  from  $\text{Cr}_2\text{O}_3$  with the intermediate formation of  $\text{Cr}_2\text{O}_5$  from which  $\text{CrO}_2$  is prepared by using a modifier  $\text{Sb}_2\text{O}_3$  under elevated pressure of 390 to 520 atmos. The  $\text{CrO}_2$  has saturation magnetization of from 5000 to 56000 oersted.

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L. Ranno, J. et al, teaches the high-pressure synthesis of  $\text{CrO}_2$  films on the  $\text{Al}_2\text{O}_3$  substrate. The making of thin film is a different field of technology and though the starting material is same, the synthesis route of bulk of present method cannot be compared with it. Further the magneto resistance 0.5 % at 300 K mentioned is for the thin film.

US 3 117 093 A teaches preparation of  $\text{Cr}_x\text{O}_y$  as an intermediate for formation of  $\text{CrO}_2$ . A slurry of  $\text{Cr}_x\text{O}_y$  with  $\text{SbO}_2$  as modifier is heated under pressure of 50 to 300 atmosphere to form  $\text{CrO}_2$ . Moreover, the  $\text{CrO}_2$  has saturation magnetization of 74 to 85 emu/gm.

GB 1 343 622 A teaches process for preparing  $\text{CrO}_2$  by oxidizing chromium or passivated chromium under pressure of 5 to 300 atmospheric pressure. The saturation magnetization of the  $\text{CrO}_2$  thus obtained is between 87 to 89 emu/gm.

US 3 979 310 A teaches method of preparation of  $\text{CrO}_2$  with starting material  $\text{Cr}_2(\text{CrO}_4)_3 \cdot n\text{H}_2\text{O}$  and uses antimony or its compound as modifier and the pressure of 200 to 500 atmos.

Thus none of the prior art alone or in combination teaches substantially pure  $\text{CrO}_2$  with the saturation magnetization of at least 115 emu/gm. Also, none of the cited art teaches the present process of preparation of substantially pure  $\text{CrO}_2$  and its composites namely  $\text{CrO}_2/\text{Cr}_2\text{O}_3$  and  $\text{CrO}_2/\text{Cr}_2\text{O}_5$  wherein  $\text{CrO}_3$  is taken as the starting material, which is heated to form the intermediate  $\text{Cr}_8\text{O}_{21}$  from which  $\text{CrO}_2$ ,  $\text{CrO}_2/\text{Cr}_2\text{O}_3$  and  $\text{CrO}_2/\text{Cr}_2\text{O}_5$  are formed by temperature modulations. Unlike the cited art no modifier is used, pressure is not a control limiting parameter and the starting material and intermediate compound are different. Accordingly the present invention is novel and inventive over the cited art.

The applicants wish to amend claim 1 to restrict the saturation magnetization value to at least 115emu/gm which may be taken on record. The basis is found in the original text where it was mentioned that the value is at least 110, which implies that it could be above 110 but not below 110. Accordingly the text at page 8 is now amended to read indicate that the chromium dioxide of present invention has saturation magnetization above 110emu/gm and preferably at least 115 emu/gm. Based on the above amendment the present claim 1 is amended. The text at page 4 is also amended to distinguish the invention over Jinnabai et.al. It is now mentioned here that this art does not teach a value of saturation magnetization above 110emu/gm.

In view of the above, amended sheets 4,8 and 24 are submitted herewith. The amended sheets 4,8 and 24 are to replace the original sheets of same number.



The applicants respectfully request for a detailed substantive examination based on the above amended claims and look forward to a favourable IPER. In the instance, however, any further clarification from the applicant be needed by the Examining Authority, a further Written Opinion may be issued to enable the applicants to have the opportunity to clarify the doubts to facilitate appreciation of the invention and its claims there under.

The applicants look forward to a favourable International Preliminary Examination Report in the matter at an early date.

Sincerely yours

DR. SANCHITA GANGULI  
Applicants' Agent

Encl. Amended text pages 4, 8 and claims page 24.

assemblies leading to high production cost are the main drawbacks of above-mentioned preparative methods. It is desirable to have a preparative method, which does not need pressure as controlling parameter.

- 5 (d) The last three US patents in the above table form relevant prior art to the present invention and will be discussed after describing the present invention in detail.

10 A ferromagnetic sample is characterized by its saturation magnetization  $M_s$  at 0 K and Curie temperature  $T_c$ . The theoretical value for saturation magnetization for  $\text{CrO}_2$  is about 135 emu/gm. The best-reported value for the saturation magnetization for polycrystalline samples range from 75–87 emu/gm as reported in earlier patents (Table 2). The single crystals have shown value of the order of 108 emu/gm. The best values of  $M_s$  for polycrystalline  $\text{CrO}_2$  supplied by DuPont is from 87-110 emu/g as given in “Spin phonon coupling in rod shaped half metallic  $\text{CrO}_2$  ultra fine particles: a magnetic Raman scattering study, T Yu et al., J. Phys. Condens. Matter 15, L213, 2003 and 15 “Junction like magnetoresistance of intergranular tunneling in field aligned chromium dioxide powders”, Jianbiai Dai and Jinke Tang, Phy. Rev. B, 63, 054434 (2001).

20 It is thus noted that for bulk polycrystalline  $\text{CrO}_2$ , the value of saturation magnetization more than 110 emu/g has not been reported in earlier.

Since the saturation magnetization value ( $M_s$ ) is an important criterion for a pure ferromagnetic material, and is a test for comparing various processes, some  $M_s$  values from literature for  $\text{CrO}_2$  are given in Table 2.

composites of  $\text{CrO}_2/\text{Cr}_2\text{O}_3$  wherein a single tunable experimental parameter is needed to obtain (a), (b) and (c).

**Summary of the invention:**

According to the present invention there is provided substantially pure chromium dioxide ( $\text{CrO}_2$ ) having saturation magnetization of above 110 emu/gm and preferably at least 115 emu/gm.

The present invention also provides composites of chromium dioxide and chromium sesquioxide ( $\text{CrO}_2/\text{Cr}_2\text{O}_3$ ) having negative magnetoresistance of at least 0.5% near room temperature at 2 Tesla.

The present invention also provides composites of chromium dioxide and  $\text{Cr}_2\text{O}_5$  ( $\text{CrO}_2/\text{Cr}_2\text{O}_5$ ) having enhanced negative magnetoresistance of at least 0.5% near room temperature at 2 Tesla.

The present invention further provides a process for manufacture of half metallic ferromagnet, substantially pure chromium dioxide ( $\text{CrO}_2$ ), or composites of chromium dioxide and chromium sesquioxide ( $\text{CrO}_2/\text{Cr}_2\text{O}_3$ ) or composites of chromium dioxide and  $\text{Cr}_2\text{O}_5$  ( $\text{CrO}_2/\text{Cr}_2\text{O}_5$ ) comprising heating an intermediate oxide of chromium to a temperature of between 350 and 500°C for a period of between 1-5 hours whereby substantially pure chromium dioxide ( $\text{CrO}_2$ ), or composites of chromium dioxide and chromium sesquioxide ( $\text{CrO}_2/\text{Cr}_2\text{O}_3$ ) or composites of chromium dioxide and  $\text{Cr}_2\text{O}_5$  ( $\text{CrO}_2/\text{Cr}_2\text{O}_5$ ) are formed.

**Detailed description of the invention**

Half metallic ferromagnet, substantially pure chromium dioxide ( $\text{CrO}_2$ ) according to the present invention exhibits saturation magnetization ( $M_s$ ) of above 110 emu/gm. preferably at least 115 emu/gm. More preferably the  $M_s$  value is at least 120 emu/gm and most preferably 135 emu/gm for cold pressed sample of  $\text{CrO}_2$  and 126 emu/g for sintered pellets. As a consequence of such high purity of the sample, there is evidence of maintained spin polarization near room temperature and the chromium dioxide of the present invention exhibits negative magnetoresistance of atleast 0.5% near room temperature at 2 Tesla, preferably 2% and most preferably 5 % MR at room temperature at 2 Tesla for sintered pellet of pure  $\text{CrO}_2$ .

Composites of chromium dioxide and chromium sesquioxide ( $\text{CrO}_2/\text{Cr}_2\text{O}_3$ ) according to the present invention have enhanced negative magnetoresistance of atleast

CLAIMS

- 5 1. Substantially pure chromium dioxide ( $\text{CrO}_2$ ) having saturation magnetization of at least 115 emu/gm.
2. Chromium dioxide according to claim 1 having saturation magnetization of at least 120 emu/gm.
- 10 3. Chromium dioxide according to claim 2 having saturation magnetization of 126 emu/gm for sintered pellets.
4. Chromium dioxide according to claim 2 having saturation magnetization of 132 to 135 emu/gm for cold pressed form.
- 15 5. Chromium dioxide according to claim 1, which is in polycrystalline form.
6. Chromium dioxide according to claim 1 having negative magnetoresistance of at least 0.5% near room temperature at 2 Tesla.
- 20 7. Chromium dioxide according to claim 6 having negative magnetoresistance of at least 2% near room temperature at 2 Tesla.
8. Chromium dioxide according to claim 7 having negative magnetoresistance of about 5% near room temperature at 2 Tesla.
- 25 9. Composites of chromium dioxide and chromium sesquioxide ( $\text{CrO}_2/\text{Cr}_2\text{O}_3$ ) having negative magnetoresistance of atleast 0.5% near room temperature at 2 Tesla.
- 30 10. Composites according to claim 9, having negative magnetoresistance of atleast 2% near room temperature at 2 Tesla.